Review of SHARC 2.0 O₃ Kinetics and Spectroscopy

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A critical review of rate constants assigned to vibrational excitation and deexcitation processes for O_3 in the Strategic High Altitude Atmospheric Radiance Code (SHARC 2.0) is presented. A complete list of O_3 pure rotational and rovibrational band parameters, based on the 1991/92 version of the HITRAN data base, is included. Modifications to specific energy transfer processes used in the SHARC 2.0 scheme have been recommended based on recent experimental literature data and on recent atmospheric observations.

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REVIEW OF SHARC 2.0 O$_3$
KINETICS AND SPECTROSCOPY

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I. INTRODUCTION

The first section of this report deals with improvements to the HITRAN data base that have been implemented very recently, i.e., since the 1986 version used for SHARC 2.0 was published. The new O_3 data was obtained prior to its publication in November 1992 (Ref. 1). The new 1991/92 HITRAN data base includes many transitions that will affect calculations for nonthermal vibrational populations. Several band origin frequencies are also improved. In particular, the 9.6-10 μm region has been revised to include many new bands and hot bands. The effects of the improvements to the O_3 spectroscopic data base on SHARC calculations of O_3 radiance have not yet been quantified; however, the edges of the fundamental bands will be affected the most, since anharmonic oscillator effects shift the band centers of upper level transitions slightly away from those of the fundamental bands. For $v_3 \geq 3$, $\Delta v = 1$ emissions, we have tabulated Einstein A coefficients derived by Rawlins et al. (Ref. 2) using an anharmonic oscillator approach, since there is no information regarding those transitions in HITRAN.

There is a limited amount of experimental data pertaining to the mechanisms and rate constants for the collisional excitation and relaxation of ozone in the upper atmosphere. Many of the excitation/relaxation rate coefficients used in SHARC 2.0 for O_3 are based on a review article by W. Rawlins (1985) (Ref. 3) and references cited therein. Rawlins has continued to be active in this subject area, with two papers on the subject of vibrationally excited O_3 produced in the three-body recombination

$$O + O_2 + M \rightarrow O_3 + M \tag{1}$$

published in 1987 (Refs. 2,4). He has provided us with helpful insights into the O_3 scheme based on his interpretations of recent SPIRIT I data (Ref. 5). We have also compared Rawlins's proposed rate constants for reactive collision processes to those listed in the NASA panel recommendations of 1990 (Ref. 6) and the NIST kinetics data base (1990) (Ref. 7).

Temperature dependences of energy transfer processes involving O_3 are difficult to study due to the thermal decomposition of O_3. For reactive collision processes, the temperatures studied have been less than approximately 360 K (a temperature range more relevant to the stratosphere than the upper atmosphere). Due to the limited range of information, a $T^{1/2}$ temperature dependence was used by Rawlins [and by Spectral Sciences Incorporated (SSI), in developing SHARC 2.0] for essentially all of the O_3 energy transfer processes (except those with rate constants $\cong 10^{-11}$ cm^3 molecule^{-1} s^{-1} at

room temperature) corresponding to a reaction probability based only on the number of collisions.

After reviewing the rate expressions used in SHARC 2.0 for collisional relaxation of O_3, we are still confused by the apparent extrapolation of a rate constant for the intermode energy transfer from (001),(100)-(010) to many other vibration-to-translation (V-T) processes, including several where only a quantum of energy from the v_3 mode was relaxed. The references provided by SSI for this assumption refer to extrapolations based on the harmonic oscillator approximation in the SSH treatment of vibrational relaxation rates. However, the extrapolations made within the SHARC 2.0 O_3 scheme are not within the scope of the theory. In order to remedy the current SHARC 2.0 scheme, it appears that first (100), (001)-(000) V-T processes should be put back into the list, with estimated rate constants. The SHARC 2.0 treatment of this aspect of the O_3 scheme is very different from that of Rawlins (Ref. 3), who used the standard treatment of multiplying the (001)-(000) rate constant by v for upper level relaxation processes to $v-1$.

One additional mechanism, involving the excitation of $O_3(102)$ and (101), seems to be necessary in SHARC in order to account for the SPIRE rocket observations and laboratory observations of Rawlins et al. (Refs. 2,4,5). A change that would make the distinction between O_2 and N_2 as collision partners for the O_3 (100,001)-(010) is suggested in Section III of this report. After reassigning rate constants to the V-T one-quantum energy transfer processes of the lowest vibrational levels, the rest of the O_3 scheme involving higher vibrational levels up to $v_3 = 9$ can be dealt with.

A listing of the current (SHARC 2.0) O_3 scheme is provided in Appendix A. The listing was provided by SSI and differs from the module actually in the code only by the inclusion of references. This scheme represents one possible way of handling excitation and relaxation mechanisms within the complex array of O_3 vibrational energy levels. We suggest some changes that may or may not be compatible with the overall assumptions made in the SSI scheme. Other updates that we suggest in this report should be relatively easy to incorporate into SHARC 3.0.

II. EINSTEIN A COEFFICIENTS

The most fundamental addition that can be made to the SHARC O_3 file is a revised list of vibrational bands and their spontaneous emission coefficients. There have been many improvements and additions to the HITRAN data base for O_3 since the 1986 version was published. The improvements were achieved by a concerted effort of investigators, who spent a considerable amount of time on improving the assignments and band strengths for the 1991 HITRAN listing. A publication describing the 1991/92 HITRAN data base can be found in the Journal of Quantitative Spectroscopy and Radiative Transfer (Ref. 1). The contributors to the O_3 section are referenced therein. HITRAN 91/92 contains 57 rovibrational bands for the main 666 isotope of O_3 and nine sets of pure rotational lines, in contrast to HITRAN 1986, which contained only 16 rovibrational bands and one set of pure rotational transitions within the (000) manifold. Many of the improvements to HITRAN are relevant to SHARC. For example, v_0 for the (003)-(000) band has been reassigned as 3046.0082 cm^{-1} rather than the previous value of 3041.200 cm^{-1}. These types of improvements will necessitate changes in the O3STAT.DAT file of SHARC as well as in the O3KIN.DAT file. Some of the band strengths previously estimated in SHARC, such as that of the (200)-(100) transition, have now been included in HITRAN. The Einstein A coefficient for that transition was previously given as 1.18 s^{-1} in SHARC 2.0, whereas using the new HITRAN band strength, A is calculated to be 0.640 s^{-1}. This is nearly a 100% decrease in the probability for spontaneous emission from that band, which occurs at 8.62 μm. The (003)-(001) A value has changed from 1.03 s^{-1} to 0.571 s^{-1}. The overall effect that the updates will have on radiance calculations performed with SHARC has not yet been quantified, and many of the "new" transitions occur from vibrational levels that will only be populated under very non-LTE conditions. However, since the code requires that levels up to as high as $v_3 = 9$ be populated, all of the additional transitions should be included. A listing of all the O_3 bands listed in HITRAN 91/92 (Ref. 1) is given in Table 1 with notations indicating changes from the 1986 listing and/or from SHARC 2.0.

Band origins and Einstein A coefficients for observed $\Delta v_3 = 1$ transitions have been reported by Rawlins et al. (Ref. 4) from experiments in which vibrationally excited O_3 was generated by reaction (1). The chemiluminescence from product $O_3(v)$ was observed at relatively high resolution and at low rotational temperatures. The band centers retrieved from the best fits to the experimental data are given in Table 1B.

Table 1: Einstein A coefficients for O_3

A: From the HITRAN data base 1991/92 Edition (Ref. 1)

v_0 (μm)	v_0 (cm^{-1})	v' - v"	Σ S cm^{-1}/(molecule-cm^{-2})	A (s^{-1})
*164	61.0533	100 - 001	2.039E-22	0.00035
*144	69.7394	110 - 011	1.514E-24	0.00028
29.31	341.1529	001 - 010	1.001E-21	0.0033
24.86	402.2062	100 - 010	2.823E-24	0.000012
16.04	623.3852	011 - 100	2.521E-23	0.0017
14.68	681.4119	021 - 011	1.958E-22	0.314
14.61	684.4385	011 - 001	3.596E-21	0.209
14.49	690.3148	120 - 110	1.181E-22	0.272
14.43	693.1246	110 - 100	2.624E-21	0.210
14.32	698.3415	020 - 010	3.879E-20	0.445
14.27	700.9311	010 - 000	5.921E-19	0.227
13.26	754.1779	110 - 001	2.461E-23	0.0017
10.75	929.8447	012 - 110	3.290E-23	0.096
10.47	954.7535	002 - 100	3.266E-21	0.483
10.11	988.9772	111 - 110	2.102E-21	9.68
10.00	999.5841	012 - 011	5.996E-21	20.09
9.92	1007.6470	101 -100	6.246E-20	10.27
9.91	1008.6618	021 - 020	1.497E-20	10.40
9.87	1015.8068	002 - 001	1.680E-19	20.83
9.75	1025.5914	011 - 000	4.635E-19	11.17
9.60	1042.0840	001 - 000	1.413E-17	11.56
9.45	1058.7166	111 - 011	6.379E-23	0.239
9.36	1068.7003	101 - 001	5.238E-21	0.719
9.20	1087.3041	120 - 020	2.207E-22	0.178
9.18	1089.9162	210 - 110	3.331E-23	0.146
9.13	1095.3308	110 - 010	1.273E-20	0.349
9.11	1098.0179	200 - 100	3.299E-21	0.642
9.07	1103.1372	100 - 000	5.403E-19	0.498
8.62	1159.0712	200 - 001	8.340E-21	1.34
8.62	1159.6556	210 - 011	1.652E-22	0.742
7.37	1356.9597	002 - 010	2.064E-23	0.00087
7.15	1399.2726	020 - 000	4.499E-22	0.0007
7.09	1409.8532	101 - 010	9.927E-22	0.045
5.86	1707.0034	021 - 010	3.421E-21	0.227
5.79	1726.5225	011 - 000	5.357E-20	0.120
5.60	1785.6456	120 - 010	1.372E-21	0.100
5.57	1796.2619	110 - 000	2.374E-20	0.058
5.15	1942.9509	003 - 100	1.379E-21	0.837
5.05	1980.5651	102 - 100	3.838E-22	0.242
4.99	2004.0042	003 - 001	1.189E-21	0.571
4.94	2025.1755	012 - 010	3.156E-21	0.295
4.90	2041.6184	102 - 001	1.562E-20	7.78
4.86	2057.8908	002 - 000	1.120E-19	0.358
4.80	2083.2724	201 - 100	1.049E-20	7.32
4.80	2084.3080	111 - 010	4.083E-20	4.04
4.74	2110.7843	101 - 000	1.236E-18	4.15

Table 1A (cont.):

v_0 (μm)	v_0 (cm^{-1})	v' - v"	Σ S	A (s^{-1})
4.66	2144.3257	201 - 001	4.579E-22	0.252
4.58	2185.2470	210 - 010	7.633E-22	0.083
4.54	2201.1552	200 - 000	3.371E-20	0.123
4.15	2407.9345	021 - 000	4.188E-22	0.0018
4.02	2486.5766	120 - 000	3.842E-22	0.0018
3.67	2726.1066	012 - 000	3.301E-21	0.0185
3.59	2785.2391	111 - 000	2.425E-20	0.142
3.46	2886.1781	210 - 000	1.101E-21	0.0069
3.28	3046.0882	003 - 000	1.312E-19	0.918
3.24	3083.7024	102 - 000	1.265E-20	0.091
3.14	3186.4097	201 - 000	9.300E-21	0.071
		011-110	1.447E-24	
		001-100	1.287E-22	
		000-000	4.470E-19	
		010-010	1.449E-20	
		001-001	2.564E-21	
		100-100	1.871E-21	
		020-020	4.582E-22	
		011-011	8.359E-23	
		110-110	5.564E-23	

a)*outside the wavelength region considered in SHARC 2.0

Table 1B: From Rawlins and Armstrong (Ref. 2) anharmonic oscillator treatment.

v_0 (μm)	v_0 (cm^{-1})	v' - v"	A (s^{-1})
9.60	*1042*	*001-000*	*11.(2)*
9.84	*1016*	*002-001*	20.7
9.92	*1008*	*101-100*	*6.0***
10.13	987	003-002	28.5
10.30	971	102-101	17.5
10.50	952	004-003	34.4
10.65	939	103-102	24.0
10.92	916	005-004	38.5
11.06	904	104-103	28.5
		006-005	40.0
		105-104	31.5
		007-006	40.9
		106-105	33.0

b) *italics* indicate transition listed in HITRAN
c) ** A significantly different from HITRAN

The five quantum level of v_3 was the highest observed in Rawlins's experiments; however, higher levels may not have been observed due to weaker intensities or resolution limitations. The authors discuss the possibility of detecting emissions from levels of v_3 greater than 5 (which emit between approximately 11 and 12 μm) in the upper atmosphere where number densities are low. Rawlins reports that recently analyzed SPIRIT I data (Ref. 5), which are of higher resolution than earlier field measurements (Ref. 8), correspond well to the experimental data, with approximately the same transitions observed (Ref. 2). For the higher v_3 transitions, the Einstein A coefficients in Table 1B were obtained from functions plotted in Reference 4, which take into account the anharmonicity of the oscillator. For $v_3 > 3$, the A values are reported to be upper bounds. Rawlins's anharmonic oscillator estimation of the Einstein A coefficients is a better one than a simple harmonic oscillator treatment. It is unclear where the corresponding coefficients in SHARC 2.0 came from. If they were calculated from an anharmonic oscillator function based on lower transitions listed in the HITRAN data base, they are probably satisfactory, but they would need to be updated using HITRAN 91/92 for the basis of the calculation. It is certain that they were not taken directly from Rawlins's original review (Refs. 9,10).

Finally, two bands not listed at all in the HITRAN data base are included in SHARC 2.0. In the code a rate constant for the hypothetical transition (111)-(001) is equated to the (110)-(000) value, and a second hypothetical transition (111)-(100) is assigned a rate constant from the (011)-(000) band. We have not found any published observations or measurements for these two transitions from the (111) level. There is no obvious reason for creating them, since another transition, (111)-(010), has a relatively strong Einstein A coefficient, providing at least one relaxation channel from that level. On the other hand, several bands not included in SHARC 2.0 are listed in Table 1. For a more complete spectral picture of the 9-10 μm region, these additional bands in particular should be included in SHARC.

III. COLLISIONAL EXCITATION OF O_3

A. EXCITATION VIA $O + O_2 + M \rightarrow O_3(v) + M$

The NIST Chemical Kinetics Database (1990) (Ref. 7) has 37 references to kinetic data for this reaction over the temperature range of approximately 200-360 K (see Figure 1). The rate constant exhibits a steep negative temperature dependence. The rate coefficients reported in such data bases as NIST or the NASA panel evaluation are for the total thermal reaction. Presumably the product distribution is over all $O_3(v)$ states formed, and the rate constant, therefore, refers to a summation over all product states.

Early laboratory experiments (Ref. 11) indicated that the excitation of $O_3(v)$ via process (1) was predominantly in the stretching modes. In the most recent experiments conducted by Rawlins et al. (Ref. 2), a further attempt was made to sort out the kinetics as a function of the final state distribution. The approach taken by Rawlins (Refs. 2,3) was to use a "prior" distribution of states according to surprisal theory to calculate the population probability factors,

$$P^0(v) = \frac{(1-E_v/E)^{3/2}}{\sum_v (1-E_v/E)^{3/2}} \tag{2}$$

given the total energy E available to the system. The experimental work by Rawlins (1987) appears to substantiate this treatment, used first in his 1985 review and later in SHARC 2.0. The final conclusion (Refs. 2-4) is that the energy distribution of the product $O_3(v)$ formed in process (1) is rapidly randomized throughout the asymmetric stretching mode $O_3(v_3)$.

To obtain the appropriate rate constants for each of the $O_3(v_3)$ products, Rawlins (Ref. 3) used the rate expression for the *total* reaction of

$$O + O_2 + N_2 \rightarrow O_3(\Sigma v_3) + N_2 \tag{3}$$

from the work of Huie et al. (Ref. 12),

$$k_{total} = 1.1 \times 10^{-34} e^{510/T} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \tag{4}$$
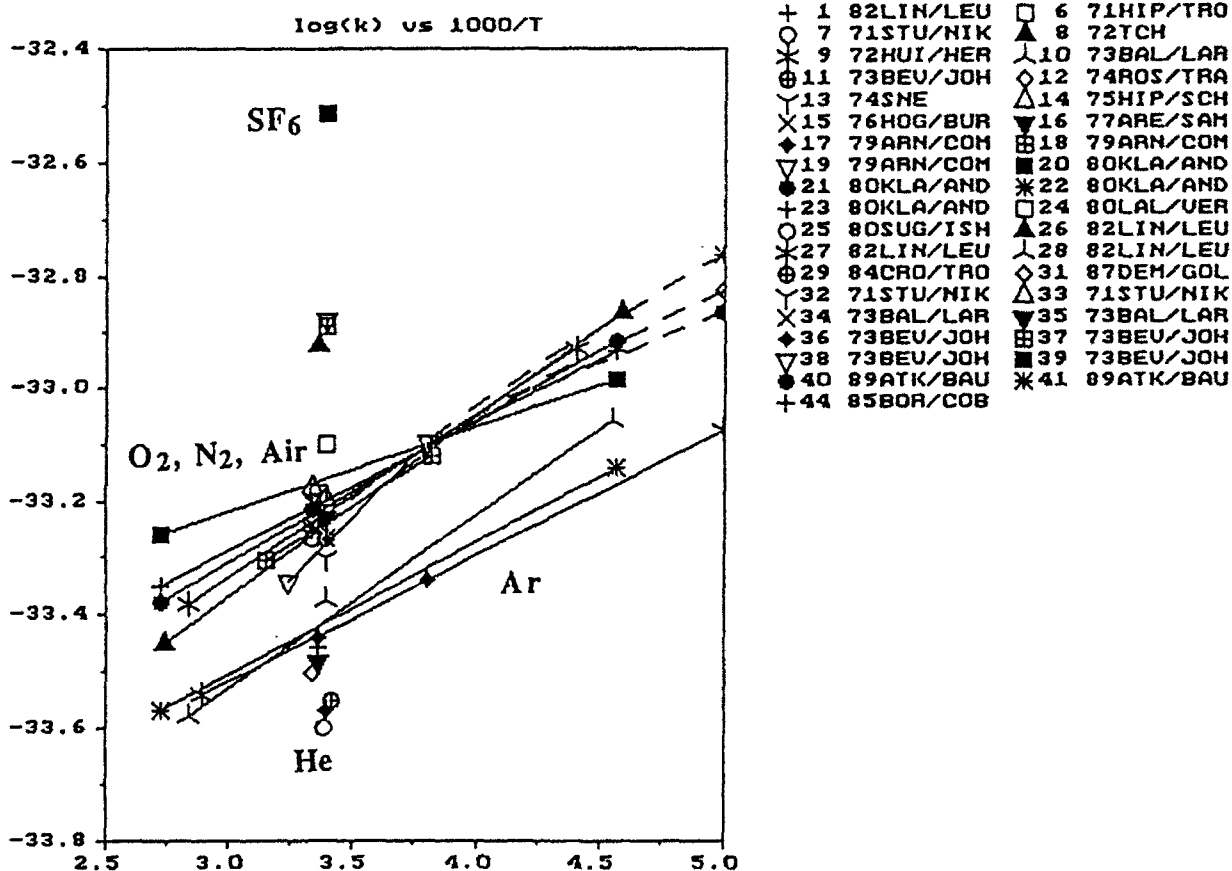
Figure 1: Rate constant data for $O + O_2 + M \rightarrow O_3 + M$ from the NIST Data Base, for various collision partners, M. The data set labeled 31 corresponds to the NASA panel recommendation (unchanged from 1987 to 1990 versions). The data set labeled 9 (Huie et al.) was depicted for M = Ar. Their results for M = O_2 lie in the middle of the O_2, N_2, air data.

and multiplied it by the relative population of each of the excited vibrational levels obtained from expression (2). At 300 K, the rate constant calculated from the expression reported by Huie et al. for M = N_2 is essentially the same as the value calculated from the expression recommended by the NASA panel for M = air,

$$k_{total} = 6 \times 10^{-34} (T/300)^{-2.3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \tag{5}$$

From Eqs. (5) and (6), the 300 K rate constant is 6×10^{-34} cm^6 molecule^{-2} s^{-1}. In the Arrhenius plot from the NIST data base, given in Figure 1, the expression of Huie et al. is linear, while that of the NASA panel is nonlinear. Both sets of data fall within the "average" data for the reaction with M = air, O_2, or N_2. In Figure 2, rate constants obtained from expressions (4) and (5) in addition to a linear fit through the data recommended by the NASA panel,

$$k_{total} = 9.27 \times 10^{-35} e^{562/T} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}, \tag{6}$$

are plotted as a function of T. Unfortunately, none of these expressions was intended to be extrapolated to temperatures above approximately 360 K. From Figure 2, it is obvious that the two different functional forms (linear and nonlinear in terms of log(k) and 1000/T) start to deviate sharply as the temperature is increased.

The conclusion from this analysis is that for atmospheric temperatures less than approximately 360 K, either the single data set of Huie et al. or a selective average of data reported for M = air are nearly equivalent. However, as temperatures approach 400 K and above, a large difference in rate constants occurs depending on the choice of the function for the temperature dependence. This should be considered more carefully if, for example, auroral temperatures in the upper atmosphere are substituted into expression (4) in SHARC.

B.   ADDITIONAL EXCITATION MECHANISMS

From data obtained in microwave discharge experiments (Refs. 2,4) and from SPIRIT I (Ref. 5), Rawlins found evidence for O_3 (101) and (102) transitions involving one quantum of v_3. In the laboratory work, evidence for the population of the higher stretch combination levels (103) and (104) was also found. A resonant V-V energy exchange with O_2 (v = 2) has been proposed to account for the population of (102), which
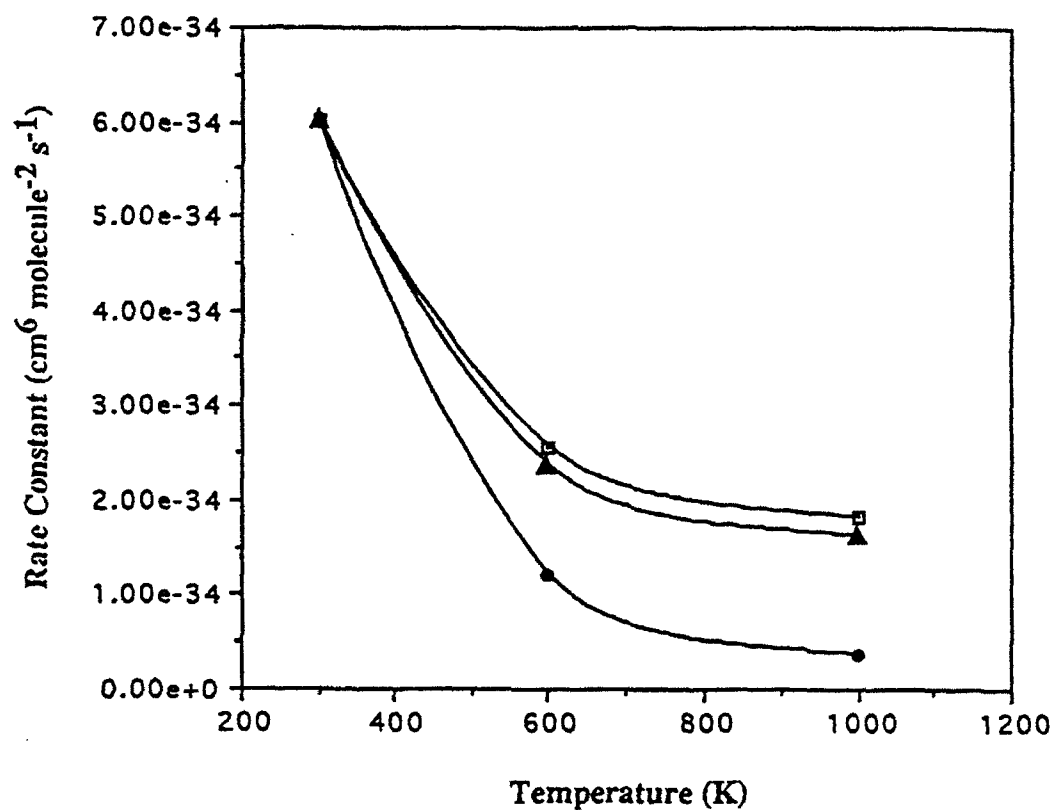
□ Huie et al., ($M = N_2$), Linear Arrhenius function (4)

● NASA Panel Evaluation, non-linear function (5)

▲ NASA Panel Evaluation, linear Arrhenius function (6)

Figure 2: Temperature dependence of rate constants for
$$O + O_2 + M \rightarrow O_3 + M$$

can be followed by relaxation to (101). The (101) level can then radiate, or undergo an energy transfer process. The possible sequence of reactions is

$$O_2(v = 2) + O_3(000) \rightarrow O_2(v = 0) + O_3(102) \tag{7}$$
$$O_3(102) + M \rightarrow O_3(101) + M \tag{8}$$
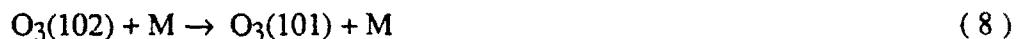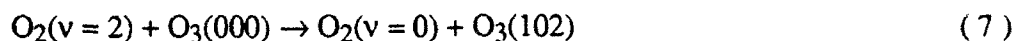
Rawlins et al. also report that it is likely that $O_3(003)$ and subsequently $O_3(002)$ are enhanced to some extent by the deactivation of $O_3(102)$. With respect to SHARC calculations, the inclusion of steps (7) and (8) will not have much effect on the overall radiance, but the fine structure of calculated spectra will be affected.

Rawlins suggests that population of the (103) and (104) states in the laboratory experiments occurred by rapid, near resonant V-T transfer from $O_3(004)$ and (005) formed in reaction (1); however, this thermalization may have been specific to the laboratory experiments. Two other mechanisms described in Reference 2 for population of combination levels by electronically excited O_2, or by energetic electrons, are also more relevant to the discharge experiments than to atmospheric conditions.

IV. COLLISIONAL RELAXATION PROCESSES FOR $O_3(v)$

Before discussing some of the individual rate constants for collisional relaxation of $O_3(v)$ by O_2, N_2, and O, some assumptions made in the overall scheme used in SHARC 2.0 should be examined. The scheme does not include the processes

$$O_3(001) + M' = O_3(000) + M' \quad M' = O_2, N_2 \text{ or } O \quad (9)$$
$$\text{and} \quad O_3(100) + M' = O_3(000) + M' \quad M' = O_2, N_2 \text{ or } O \quad (10)$$
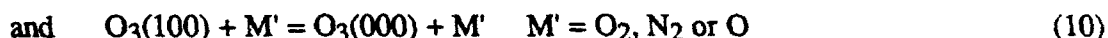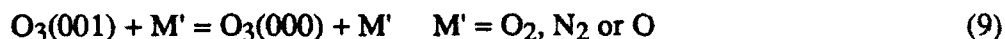
While the v_1 and v_3 fundamental bands are weaker than the v_2 band, this doesn't mean that Processes (9) and (10) may be eliminated. [This aspect of the SHARC 2.0 scheme was not based on Rawlins's review, since (9) *is* included in his scheme.] If one assumes that the (100) and (001) levels rapidly equilibrate, then possibly the (001) V-T channel, given in Eq. (9), can be used to represent both pathways (9) and (10). However, an inconsistency exists in the SHARC 2.0 scheme because processes are itemized for both (100) and (001) transfer to (010). This wouldn't be necessary if all the (100) energy relaxes through the (001) level. In the actual experiments done to date, it has not been possible to distinguish between relaxation from (001) and (100).

Even though very little data exists regarding the direct V-T relaxation from (001, 100), the rate constant has been measured with O_3 as the collision partner (Refs. 13,14). Furthermore, the upper limit for the rate constant for processes (9) and (10), where $M = O_2$ and N_2, is reported to be approximately 1/10 that of the V-T relaxation from $O_3(010)$ (Ref. 14). These processes are therefore not necessarily negligible.

Keeping the omission of processes (9) and (10) in mind, the most confusing part of the SHARC 2.0 scheme is that all $O_3(00v)-(00v-1)$ V-T rate constants are set equal to multiples of the $O_3(001)-(010)$ rate constant. For example, the rate constant for

$$O_3(005) + M = O_3(004) + M \qquad k = 1.45 \times 10^{-14} T^{1/2} \qquad (11)$$

is set equal to 5 times the rate constant for

$$O_3(001) \text{ or } (100) + M = O_3(010) + M \qquad k = 2.89 \times 10^{-15} T^{1/2}. \qquad (12)$$

Normally, the fundamental process involving relaxation of one quantum of energy from the same vibrational mode would be used as the basis for the extrapolation. The references given by SSI in Appendix A, SHARC 2.0, do not explain the assumptions made here.
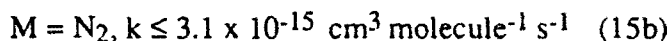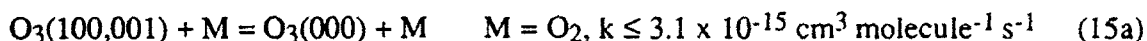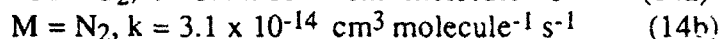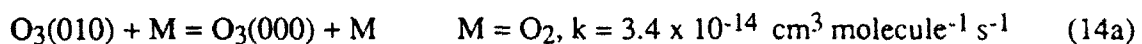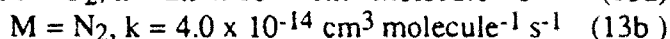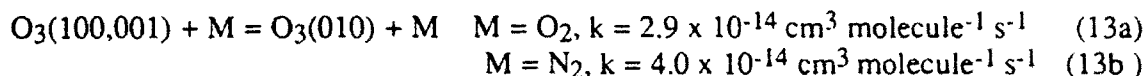
Since processes (11) and (12) involve transfer or exchange of different types of vibrational quanta, the extrapolation of the rate constant for (11) to that for (12) seems unusual. In SHARC 2.0 the assumption that the rate constant for relaxation of one quantum of v_3 energy should correspond to that for process (12) was used for 10 more processes in which a quantum of energy from one mode of a combination level was relaxed down to a fundamental level. Since the processes listed did not involve energy exchange between the stretch and bend modes, it again seems unusual that the rate constant for process (12) was extrapolated to so many different pathways in the SHARC 2.0 scheme.

The use of only the (00v) part of the ladder of vibrational levels in SHARC 2.0 appears to be an artificial way of relaxing the upper levels to the fundamentals without including the many intermode energy transfer pathways available between the stretch and the bend modes. This is somewhat inconsistent with the inclusion of energy transfer processes from both (100) and (001) to (010) at the fundamental level. If the approximation of only using part of the ladder is a good one, then the approximation that the conversion of (100) to (001) is rapid and essentially complete in one direction should also be maintained.

The potential errors associated with making inconsistent assumptions, such as those described above, are compounded when M = O. Since very little experimental data are available for O as the collision partner for O_3 relaxation, most of the rate constants associated with O in SHARC 2.0 are approximations obtained by multiplying the rate constant for a comparable process involving N_2 or O_2 by 100. Specifics of the processes where M = O are discussed in Section IIIB.

A.   COLLISIONAL RELAXATION OF $O_3(v)$ WITH M = N_2 OR O_2

Recent infrared double resonance studies by Menard-Bourcin, Menard, and Doyennette (Refs. 13-15) (1989-1990) have provided measurements specific to N_2, O_2, Ar, and O_3 as collision partners in the relaxation of vibrationally excited $O_3(100, 001)$ and $O_3(010)$. The error bars associated with their results are significantly improved over those of earlier measurements, particularly those of West, Weston, and Flynn (1976) (Ref. 16). One significant feature of the experiments performed by Menard-Bourcin et al. (Ref. 14) is that measurements were actually made with N_2. While O_2 and Ar apparently behave similarly in most interactions with O_3, the intermode transfer between $O_3(100,001)$ and $O_3(010)$ occurs ~ 40% faster with M = N_2 than with M = O_2. The six relevant processes for which Menard-Bourcin et al. (Ref. 14) have provided new data are as follows:

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$$O_3(100,001) + M = O_3(010) + M \quad M = O_2, k = 2.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (13a)$$
$$M = N_2, k = 4.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (13b)$$

$$O_3(010) + M = O_3(000) + M \quad M = O_2, k = 3.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (14a)$$
$$M = N_2, k = 3.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (14b)$$

$$O_3(100,001) + M = O_3(000) + M \quad M = O_2, k \leq 3.1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (15a)$$
$$M = N_2, k \leq 3.1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (15b)$$

Several other papers describing work in this area were previously published. Joens, Burkholder, and Bair (Ref. 17) used a somewhat indirect method for extracting rate constants from vibrational population distributions from vibrational spectra of O_3, which may have resulted in their anomalous (100,001) to (010) rate constant. West, Weston, and Flynn (Ref. 16) have assigned a large uncertainty to that rate constant. Beyond that, the choice of which of the rate constants with $M = O_2$ are best is somewhat subjective. Averaging the values of the three most reliable works–Adler-Golden and Steinfeld (Ref. 18), West, Weston, and Flynn (Ref. 16), and Menard-Bourcin et al. (Ref. 14)–for the $M = O_2$ processes, would make the difference between $M = O_2$ and $M = N_2$ indiscernible. Based on the many detailed and reliable experiments published by Doyennette et al. for other vibrational relaxation systems, we would suggest simply using their rate constants for the first four processes listed above. An efficiency coefficient to differentiate between $M = N_2$ and $M = O_2$ could be used in the SHARC kinetics module.

B. COLLISIONAL ENERGY TRANSFER FROM O_3 (v) TO O ATOMS

At altitudes up to ~ 120 km, O_2 and N_2 rather than O will be the predominant collision partners for $O_3(v)$. Above that altitude atomic O begins to predominate, but the O_3 number density decreases very rapidly. Therefore, accurate assumptions regarding rate constants for relaxation processes involving O are somewhat less important than for $M = O_2$ or N_2. There are, however, some modifications that would make the SHARC scheme more consistent.

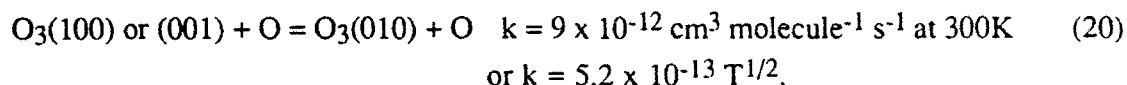Both a reactive and a nonreactive channel are possible when $O_3(v)$ collides with O, namely,

$$O_3(v) + O \rightarrow O_2 \quad (16)$$
$$O_3(v) + O \rightarrow O_3(v-1) + O \quad (17)$$

The kinetic data pertaining to the relaxation of $O_3(100)$, (001), and (010) by $O(^3P)$ are less conclusive than for V-T relaxation by N_2 and O_2. Two papers by West et al. (Refs. 16,19), dating from 1976 and 1978, were referenced with respect to the $O_3 + O(^3P)$ process in the review article by Rawlins (Ref. 3). It appears, however, that the conclusions drawn by Rawlins were based solely on the earlier work. In the latter paper, West et al. showed that the chemical reaction channel (16) is a minor one compared to the nonreactive relaxation pathway (17). In SHARC 2.0 and in Rawlins's review, it is assumed that all of the reactive channels originate from $(00v)$ and that all of the V-T relaxation to the ground level proceeds from (010), i.e.,

$$O_3(00v) + O \rightarrow O_2 \tag{18}$$
$$O_3(010) + O \rightarrow O_3 + O. \tag{19}$$

In their latter paper, West et al. (Ref. 19) reported that at least 70% of the O_3 deactivation occurred via the nonreactive channel (17) and that the upper limit for the rate constant of (16) is 4.5×10^{-12} cm^3 molecule^{-1} s^{-1}, with a total rate constant for both (18) and (19) of 10^{-11} cm^3 molecule^{-1} s^{-1}. In contrast to this, a rate constant for all reactive processes (18) where $v \leq 9$, of 1×10^{-11} cm^3 molecule^{-1} s^{-1}, is used in SHARC 2.0. This rate constant appears to be based on an early approximation by West et al. (Ref. 16), which was used in Rawlins's review (Ref. 3). This interpretation, used in SHARC 2.0, contradicts the later work of West et al., since it would mean that the rate constant for (19) is zero, and they found that approximately 70% of the reaction went by that pathway. Furthermore, it is likely that the reaction rate constant increases with increasing vibrational excitation of O_3, and that using a rate constant which is fast or approaching gas kinetic for the lowest reactant level O_3 ($v = 1$) limits how much the rate constant for higher energy levels can be increased. In order to define a lower limit for the rate constant of the reactive pathway (18), we considered the literature data for the thermal $O_3 + O(^3P) \rightarrow O_2 + O_2$ process. The NASA panel review and the NIST data base report that the reaction proceeds with a rate constant of approximately 8×10^{-15} cm^3 molecule^{-1} s^{-1} at room temperature (Refs. 6,7). All of these references indicate that the rate constant for reaction (18) with $v_3 = 1$ is actually smaller than the value of 1×10^{-11} currently in SHARC 2.0 and favored by Rawlins. We recommend that a value of approximately 4.5×10^{-12} (i.e., the upper limit) be used for the rate constant of (18) when $v = 1$ and that the value be scaled with increasing v. We consider next the rate constant for (19). In SHARC 2.0, the rate constant for relaxation of the (010) level when $M = O_2$ or N_2 was simply multiplied by 100

to obtain a value of 3×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K for (19). Coincidentally, this would be consistent with our suggestion of reducing the rate constant for (18) so that the rate constants for (18) and (19) totaled less than 1×10^{-11} cm^3 molecule^{-1} s^{-1}. Therefore, the rate expression for (19) could be left as it is.

In the list of references furnished to us by SSI, the rate constant for the energy transfer from either of the stretching modes to the bend,

$$O_3(100) \text{ or } (001) + O = O_3(010) + O \quad k = 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300K \qquad (20)$$
$$\text{or } k = 5.2 \times 10^{-13} \text{ T}^{1/2}.$$

is referenced to the 1976 paper by West et al. The value of approximately 10^{-11} cm^3 molecule^{1} s^{-1} is basically an assumption made in order to substantiate the two-step relaxation pathway, (001, 100)-(010)-(000), for which the latter step is presumably rate limiting. A value of 3×10^{-12} cm^3 molecule^{-1} s^{-1} for the rate constant of the second step, process (19), is used in SHARC 2.0. After examination of the SHARC 2.0 scheme, it is not clear why the assumption about the rate constant for (20) is multiplied and extrapolated many more times in the scheme for processes that involve V-T relaxation of v_3 rather than an intermode energy transfer. Again, there is no (100) or (001) V-T transfer to (000) listed in the SHARC 2.0 scheme for M = O, which would seem a more logical basis for extrapolations to processes involving higher vibrational levels. This is analogous to the extrapolations for M = O$_2$ and N$_2$ discussed at the beginning of this section.

C. TEMPERATURE DEPENDENCES OF THE RATE CONSTANTS FOR NONREACTIVE COLLISIONAL RELAXATION PROCESSES

There are no experimental data available for the temperature dependences of nonreactive collisional relaxation processes of vibrationally excited O$_3$. For the most part, Rawlins (Ref. 3) assumed a T$^{1/2}$ function, based on a simple increase in the number of collisions as the temperature is increased. Predicting different slopes for the temperature dependences is difficult without further experimental data at temperatures higher than room temperature.

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APPENDIX A

This appendix contains a listing of the current O_3 scheme used in SHARC 2.0. It was prepared by Spectral Sciences Incorporated, and they have provided the references at the end of the table.

TABLE A1. REACTIONS AND RATE CONSTANTS FOR O_3 MODEL

Reaction	Rate Constant*	Reference
$O + O_2 + M \rightarrow O_3(000) + M$	$2.79 \times 10^{-35} e^{510.0/T}$	a,b
$O + O_2 + M \rightarrow O_3(001) + M$	$2.35 \times 10^{-35} e^{510.0/T}$	a,b
$O + O_2 + M \rightarrow O_3(002) + M$	$1.85 \times 10^{-35} e^{510.0/T}$	a,b
$O + O_2 + M \rightarrow O_3(003) + M$	$1.42 \times 10^{-35} e^{510.0/T}$	a,b
$O + O_2 + M \rightarrow O_3(004) + M$	$1.06 \times 10^{-35} e^{510.0/T}$	a,b
$O + O_2 + M \rightarrow O_3(005) + M$	$7.59 \times 10^{-36} e^{510.0/T}$	a,b
$O + O_2 + M \rightarrow O_3(006) + M$	$4.73 \times 10^{-36} e^{510.0/T}$	a,b
$O + O_2 + M \rightarrow O_3(007) + M$	$2.53 \times 10^{-36} e^{510.0/T}$	a,b
$O + O_2 + M \rightarrow O_3(008) + M$	$8.80 \times 10^{-37} e^{510.0/T}$	a,b
$O + O_2 + M \rightarrow O_3(009) + M$	$2.20 \times 10^{-37} e^{510.0/T}$	a
$O_3(010) + M = O_3(000) + M$	$1.73 \times 10^{-15} T^{1/2}$	c
$O_3(010) + O = O_3(000) + O$	$1.73 \times 10^{-13} T^{1/2}$	d
$O_3(020) + M = O_3(010) + M$	$3.46 \times 10^{-15} T^{1/2}$	e
$O_3(020) + O = O_3(010) + O$	$3.46 \times 10^{-13} T^{1/2}$	e
$O_3(100) + M = O_3(010) + M$	$2.89 \times 10^{-15} T^{1/2}$	c
$O_3(100) + O = O_3(010) + O$	$5.20 \times 10^{-13} T^{1/2}$	d
$O_3(100) + M' = O_3(001) + M'$	1.00×10^{-11}	b,c
$O_3(200) + M = O_3(100) + M$	$5.80 \times 10^{-15} T^{1/2}$	e
$O_3(200) + O = O_3(100) + O$	$1.04 \times 10^{-12} T^{1/2}$	e
$O_3(200) + M' = O_3(101) + M$	1.00×10^{-11}	f
$O_3(001) + M = O_3(010) + M$	$2.89 \times 10^{-15} T^{1/2}$	c
$O_3(001) + O = O_3(010) + O$	$5.20 \times 10^{-13} T^{1/2}$	d
$O_3(002) + M = O_3(001) + M$	$5.80 \times 10^{-15} T^{1/2}$	e
$O_3(002) + O = O_3(001) + O$	$1.04 \times 10^{-12} T^{1/2}$	e
$O_3(003) + M = O_3(002) + M$	$8.70 \times 10^{-15} T^{1/2}$	e
$O_3(003) + O = O_3(002) + O$	$1.56 \times 10^{-12} T^{1/2}$	e
$O_3(004) + M = O_3(003) + M$	$1.16 \times 10^{-14} T^{1/2}$	e
$O_3(004) + O = O_3(003) + O$	$2.08 \times 10^{-12} T^{1/2}$	e
$O_3(005) + M = O_3(004) + M$	$1.45 \times 10^{-14} T^{1/2}$	e

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Reaction	Rate Constant*	Reference
$O_3(005) + O = O_3(004) + O$	$2.60 \times 10^{-12} T^{1/2}$	e
$O_3(006) + M = O_3(005) + M$	$1.74 \times 10^{-14} T^{1/2}$	e
$O_3(006) + O = O_3(005) + O$	$3.12 \times 10^{-12} T^{1/2}$	e
$O_3(007) + M = O_3(006) + M$	$2.03 \times 10^{-14} T^{1/2}$	e
$O_3(007) + O = O_3(006) + O$	$3.64 \times 10^{-12} T^{1/2}$	e
$O_3(008) + M = O_3(007) + M$	$2.32 \times 10^{-14} T^{1/2}$	e
$O_3(008) + O = O_3(007) + O$	$4.16 \times 10^{-12} T^{1/2}$	e
$O_3(009) + M = O_3(008) + M$	$2.61 \times 10^{-14} T^{1/2}$	e
$O_3(009) + O = O_3(008) + O$	$4.68 \times 10^{-12} T^{1/2}$	e
$O_3(001) + O \rightarrow O_2 + O_2$	1.00×10^{-11}	b,d
$O_3(002) + O \rightarrow O_2 + O_2$	1.00×10^{-11}	b,d
$O_3(003) + O \rightarrow O_2 + O_2$	1.00×10^{-11}	b,d
$O_3(004) + O \rightarrow O_2 + O_2$	1.00×10^{-11}	b,d
$O_3(005) + O \rightarrow O_2 + O_2$	1.00×10^{-11}	b,d
$O_3(006) + O \rightarrow O_2 + O_2$	1.00×10^{-11}	b,d
$O_3(007) + O \rightarrow O_2 + O_2$	1.00×10^{-11}	b,d
$O_3(008) + O \rightarrow O_2 + O_2$	1.00×10^{-11}	b,d
$O_3(009) + O \rightarrow O_2 + O_2$	1.00×10^{-11}	b,d
$O_3(011) + M = O_3(010) + M$	$2.89 \times 10^{-15} T^{1/2}$	g
$O_3(011) + O = O_3(010) + O$	$5.20 \times 10^{-13} T^{1/2}$	g
$O_3(011) + M = O_3(001) + M$	$1.73 \times 10^{-15} T^{1/2}$	g
$O_3(011) + O = O_3(001) + O$	$1.73 \times 10^{-13} T^{1/2}$	g
$O_3(110) + M = O_3(010) + M$	$2.89 \times 10^{-15} T^{1/2}$	g
$O_3(110) + O = O_3(010) + O$	$5.20 \times 10^{-13} T^{1/2}$	g
$O_3(110) + M = O_3(100) + M$	$1.73 \times 10^{-15} T^{1/2}$	g
$O_3(110) + O = O_3(100) + O$	$1.73 \times 10^{-13} T^{1/2}$	g
$O_3(101) + M = O_3(001) + M$	$2.89 \times 10^{-15} T^{1/2}$	g
$O_3(101) + O = O_3(001) + O$	$5.20 \times 10^{-13} T^{1/2}$	g
$O_3(101) + M = O_3(100) + M$	$2.89 \times 10^{-15} T^{1/2}$	g

Reaction	Rate Constant[*]	Reference
$O_3(101) + O = O_3(100) + O$	$5.20\times10^{-13}T^{1/2}$	g
$O_3(101) + M' = O_3(002) + M'$	1.00×10^{-11}	f
$O_3(111) + M = O_3(101) + M$	$1.73\times10^{-15}T^{1/2}$	g
$O_3(111) + O = O_3(101) + O$	$1.73\times10^{-13}T^{1/2}$	g
$O_3(111) + M = O_3(011) + M$	$2.89\times10^{-15}T^{1/2}$	g
$O_3(111) + O = O_3(011) + O$	$5.20\times10^{-13}T^{1/2}$	g
$O_3(111) + M = O_3(110) + M$	$2.89\times10^{-15}T^{1/2}$	g
$O_3(111) + O = O_3(110) + O$	$5.20\times10^{-13}T^{1/2}$	g
$O_3(010) \rightarrow O_3(000) + h\nu$	0.224	h
$O_3(001) \rightarrow O_3(000) + h\nu$	11.00	h
$O_3(100) \rightarrow O_3(000) + h\nu$	0.594	h
$O_3(011) \rightarrow O_3(000) + h\nu$	0.116	h
$O_3(110) \rightarrow O_3(000) + h\nu$	0.053	h
$O_3(002) \rightarrow O_3(000) + h\nu$	0.342	h
$O_3(101) \rightarrow O_3(000) + h\nu$	3.67	h
$O_3(200) \rightarrow O_3(000) + h\nu$	0.106	h
$O_3(111) \rightarrow O_3(000) + h\nu$	0.131	h
$O_3(003) \rightarrow O_3(000) + h\nu$	0.746	h
$O_3(020) \rightarrow O_3(010) + h\nu$	0.446	h
$O_3(011) \rightarrow O_3(010) + h\nu$	10.39	h
$O_3(110) \rightarrow O_3(010) + h\nu$	0.291	h
$O_3(111) \rightarrow O_3(010) + h\nu$	3.67	h
$O_3(002) \rightarrow O_3(001) + h\nu$	20.72	h
$O_3(101) \rightarrow O_3(001) + h\nu$	0.437	h
$O_3(111) \rightarrow O_3(001) + h\nu$	0.053	h
$O_3(003) \rightarrow O_3(001) + h\nu$	1.03	h
$O_3(101) \rightarrow O_3(100) + h\nu$	9.68	h
$O_3(200) \rightarrow O_3(100) + h\nu$	1.18	h
$O_3(111) \rightarrow O_3(100) + h\nu$	0.116	h

TABLE A1. (CONTINUED)

Reaction	Rate Constant[*]	Reference
$O_3(111) \rightarrow O_3(011) + h\nu$	0.593	h
$O_3(111) \rightarrow O_3(110) + h\nu$	11.01	h
$O_3(003) \rightarrow O_3(002) + h\nu$	30.44	h
$O_3(004) \rightarrow O_3(003) + h\nu$	36.34	h
$O_3(005) \rightarrow O_3(004) + h\nu$	43.08	h
$O_3(006) \rightarrow O_3(005) + h\nu$	48.49	h
$O_3(007) \rightarrow O_3(006) + h\nu$	52.71	h
$O_3(008) \rightarrow O_3(007) + h\nu$	56.12	h
$O_3(009) \rightarrow O_3(008) + h\nu$	58.67	h

[*] Rate constants are in units of 1/s for unimolecular reactions, cm^3/molecule-s for bimolecular reactions and cm^6/molecule-s for termolecular reactions.

[a] R.E. Huie, J.T. Herron, and D.D. Davis, "Absolute Rate Constants for the Reaction of $O+O_2+M \rightarrow O_3+M$ over the Temperature Range 200-346 K," J. Phys. Chem., 76, 2653 (1972).

[b] W.T. Rawlins, "Chemistry of Vibrationally Excited Ozone in the Upper Atmosphere," J. Geophys. Res., 90, 12283 (1985).

[c] S.M. Adler-Golden and J.I. Steinfeld, "Vibrational Energy Transfer in Ozone by Infrared-Ultraviolet Double Resonance," Chem. Phys. Letters, 76, 479 (1980).

[d] G.A. West, R.E. Weston, Jr., and G.W. Flynn, "Deactivation of Vibrationally Excited ozone by $O(^3P)$ Atoms," Chem. Phys. Lett., 42, 488 (1976).

[e] Estimate based on SSH theory, $k_{n \rightarrow n-1} = nk_{1 \rightarrow 0}$.

[f] Estimate based on $k_{lmn \rightarrow l-1mn+1} = k_{100 \rightarrow 001}$.

[g] Estimate based on $k_{lmn \rightarrow lm-1n} = k_{010 \rightarrow 000}$, $k_{lmn \rightarrow l-1mn} = k_{100 \rightarrow 000}$, or $k_{lmn \rightarrow lmn-1} = k_{001 \rightarrow 000}$.

[h] L. S. Rothman, et al., "The HITRAN Database: 1986 Edition," Appl. Opt., 26, 4058 (1987).

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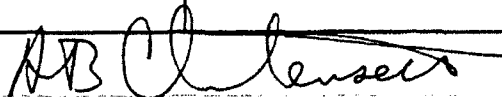
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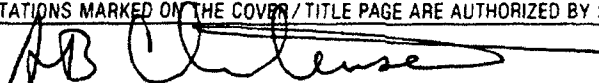| MILITARY AND GOVERNMENT OFFICES	ASSOCIATE CONTRACTORS AND OTHERS

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